

## Supporting Information for

### Decorating Metal Oxide Surfaces with Fluorescent Chlorosulfonated Corroles

Carl M. Blumenfeld<sup>§,¶</sup>, Robert H. Grubbs<sup>¶</sup>, Rex A. Moats<sup>§</sup>, Harry B. Gray<sup>§,¶,\*</sup>, and Karn Sorasaene<sup>§,¶,§\*</sup>

<sup>§</sup> Beckman Institute, California Institute of Technology, Pasadena, California 91125

<sup>¶</sup> Department of Chemistry, California Institute of Technology, Pasadena, California 91125

<sup>§</sup> Translational Biomedical Imaging Center, Department of Radiology, The Saban Research Institute, Children's Hospital Los Angeles, University of Southern California, Los Angeles, California 90027

## Experimental

**Materials.** 2 M AlMe<sub>3</sub> in toluene (Aldrich), GaCl<sub>3</sub> (Aldrich), HSO<sub>3</sub>Cl (Aldrich), 21 nm nanopowder TiO<sub>2</sub> (Aldrich), 30% H<sub>2</sub>O<sub>2</sub> (EMD) were obtained commercially and used as received. The starting material 5,10,15-tris(pentafluorophenyl) corrole (H<sub>3</sub>tpfc) was prepared based on the literature method.<sup>1</sup> The solvents pyridine and toluene were dried over a column. Acetone and dichloromethane used were both of reagent and spectroscopic grades depending on the applications.

**Chemical Preparation.** All preparations were carried out under Ar(g) atmosphere unless otherwise noted.

**1. Corrole Preparation.** Preparation of 2,17-bischlorosulfonato-5,10,15-tris(pentafluorophenyl) corrole (H<sub>3</sub>tpfc(SO<sub>2</sub>Cl)<sub>2</sub>; **1**) was performed according to the literature procedure.<sup>2</sup> The metallocorroles described in this study were prepared in the following manner.

**1.1. Preparation of 1-Al.** To the 20-mL toluene solution of 0.32 g of **1** (0.32 mmol) in a round bottom flask was added 0.8 mL of 2 M AlMe<sub>3</sub> (1.6 mmol) in toluene solution at an ice-bath temperature. The solution was stirred for 10 min followed by the addition of 1 mL anhydrous pyridine. The solution was allowed to stir for another 10 min over ice. The reaction was quenched by an addition of ice chips. The dark green solution was then extracted with CH<sub>2</sub>Cl<sub>2</sub> and washed with water. The solvent was removed *in vacuo* and the dry deep green solid was redissolved in CH<sub>2</sub>Cl<sub>2</sub> followed by filtration. The filtrate was brought to dryness to afford the dark green solid (0.098 g, 26% yield). ESI-MS (CH<sub>2</sub>Cl<sub>2</sub>): *m/z*: 1014.87 [M-H]<sup>-</sup> (Calculated for C<sub>37</sub>H<sub>6</sub>N<sub>4</sub>F<sub>15</sub>Cl<sub>2</sub>S<sub>2</sub>O<sub>4</sub>Al: 1015.88); <sup>1</sup>H-NMR (400 MHz, acetone-*d*<sub>6</sub>, ppm): δ = 9.76 (*s*, 1 H), 9.25 (*s*, 1 H), 8.97 (*d*, 1 H), 8.85 (*d*, 1 H), 8.70 (*d*, 1 H), 8.58 (*d*, 1 H); <sup>19</sup>F-NMR (376 MHz, acetone-*d*<sub>6</sub>, ppm): -138.7 (*d*, 4 F), -140.0 (*d*, 2 F), -156.9 (*t*, 1 F), -157.5 (*t*, 1 F), -158.1 (*t*, 1 F), -164.9 (*m*, 2 F), -165.3 (*m*, 2 F), -167.0 (*m*, 2 F); UV-Vis (toluene:pyridine, 95:5): λ<sub>max</sub> (ε M<sup>-1</sup> cm<sup>-1</sup>) = 436 (4.08 × 10<sup>4</sup>), 625 (7.66 × 10<sup>3</sup>) nm.

**1.2. Preparation of 1-Ga.** To a heavy-walled Schlenk flask were added 0.20 g of **1** (0.20 mmol) and 0.57 g GaCl<sub>3</sub> (3.3 mmol) under Ar(g). The flask was chilled in N<sub>2</sub>(l) and evacuated. 15 mL Degassed anhydrous pyridine (15mL) was added to the flask *via* vacuum transfer. The

flask was subsequently sealed and allowed to warm to room temperature. The reaction vessel was heated to 120 °C for 1 h. The pyridine solution was diluted with CH<sub>2</sub>Cl<sub>2</sub> and washed with water three times. The solution was then filtered through glass wool and partially concentrated for recrystallization with hexanes overnight. The product was then filtered, dried, and washed with a combination of acetone, CH<sub>2</sub>Cl<sub>2</sub>, and toluene. This filtrate collected was brought to dryness *in vacuo* to afford a dark green solid (0.092 g, 38% yield). ESI-MS (CH<sub>2</sub>Cl<sub>2</sub>:pyridine): *m/z*: 1056.81 [M-H]<sup>+</sup> (Calculated for C<sub>37</sub>H<sub>8</sub>N<sub>4</sub>F<sub>15</sub>Cl<sub>2</sub>S<sub>2</sub>O<sub>4</sub>Ga: 1057.82); <sup>1</sup>H-NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm): δ = 9.99 (*s*), 8.82 (*m*), 8.73 (*m*), 8.57 (*m*); <sup>19</sup>F-NMR (376 MHz, acetone-*d*<sub>6</sub>, ppm): -138.7 (*d*), -140.0 (*d*), -156.9 (*t*), -157.5 (*t*), -158.1 (*t*), -164.9 (*m*), -165.3 (*m*), -167.0 (*m*); UV-Vis (toluene:pyridine, 95:5): λ<sub>max</sub> (ε M<sup>-1</sup> cm<sup>-1</sup>) = 429 (1.65 × 10<sup>4</sup>), 611 (5.61 × 10<sup>3</sup>) nm.

**2. TiO<sub>2</sub> Surface activation.** To the solid TiO<sub>2</sub> nanoparticle (10 g) in a 2.0-L round bottom flask was added 1.2 L 30% H<sub>2</sub>O<sub>2</sub> solution. The milky colloidal suspension was stirred under reflux for 5 h. Upon cooling, the off-white solid was isolated from the H<sub>2</sub>O<sub>2</sub> solution by ultra-centrifugation at 4 °C and washed with copious amount of water. The activated TiO<sub>2</sub> nanoparticle (TiO<sub>2</sub>-OH) collected was dried *in vacuo* for 12 h and stored dry in a vial prior to use.

**3. Surface Conjugation.** The following general procedure was employed for the conjugation of the corroles **1**, **1-Al**, and **1-Ga** to the activated TiO<sub>2</sub> nanoparticle surface: To the mixed solids containing the activated TiO<sub>2</sub> and corrole in a 25-mL round bottom flask was charged with anhydrous pyridine. The suspension turned green immediately and was stirred under reflux before the reaction was stopped. The resulting green solid was isolated from the green solution by centrifugation and washed multiple times with dichloromethane, acetone, and deionized water until the centrifuge supernatant became colorless. The solid remained green, was dried *in vacuo*, and was stored until further use. The detailed preparation procedure for each corrole nanoconjugate is given as follows:

**3.1. Preparation of 1-TiO<sub>2</sub>.** To a 25 mL round bottom flask were added 0.32 g TiO<sub>2</sub>-OH and 0.028 g of **1** (28.1 μmol), which was subsequently cycled with argon and vacuum. After establishment of the inert atmosphere, 8 mL anhydrous pyridine was added to the flask and the reaction was set to reflux for 2 h. The resulting green solid was collected in a manner following the general centrifugation and washing procedures outlined above.

**3.2. Preparation of 1-Al-TiO<sub>2</sub>.** To a 40 mL vial was added 1.18 g TiO<sub>2</sub>-OH, which was subsequently cycled with argon and vacuum. To this flask, was added 5 mL anhydrous pyridine, followed by sonication to ensure even dispersion. In a second flask, was added 0.03 g of **1-Al** (25.5 μmol) and 7 mL anhydrous pyridine under Ar(g). This solution was stirred and then added to the TiO<sub>2</sub>-OH precursor *via* syringe. The reaction was sealed and allowed to reflux for 2 h after which, the resulting green solid was collected in a manner following the general centrifugation and washing procedures outlined above.

**3.3. Preparation of 1-Ga-TiO<sub>2</sub>.** To a 40 mL vial was added 0.84 g TiO<sub>2</sub>-OH and 0.04 g of **1-Ga** (32.8 μmol), which was subsequently cycled with argon and vacuum. After establishment of the inert atmosphere, 8 mL anhydrous pyridine was added to the flask and the reaction was set to reflux for 2 h. The resulting green solid was collected in a manner following the general centrifugation and washing procedures outlined above.

**Spectroscopies.** UV-Vis spectra were either recorded on a Carey 50 spectrophotometer or a Hewlett-Packard 8453 diode-array spectrophotometer at room temperature from samples in various solvents. IR spectra were recorded with a SensIR Durascope ATR accessory plate on a Nicolet Magna-IR spectrometer, an uncooled pyroelectric deuterated triglycine sulfate (DTGS) detector, and a KBr beamsplitter. The  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra were recorded on a Varian Mercury 300 (300 MHz for  $^1\text{H}$ ; 288 MHz for  $^{19}\text{F}$ ) spectrometer. The NMR spectra were analyzed using MestReNova (v. 6.1.1).  $^1\text{H}$  NMR measurements were referenced to internal solvents. Fluorescence spectra were measured with a Jobin-Yvonne/SPEX Fluorolog spectrometer (Model FL3-11) equipped with a Hamamatsu R928 PMT. Samples were excited at  $\lambda_{\text{ex}} = 405\text{-}430\text{ nm}$  (the Soret region), 514 nm, and 600-630 nm (Q-band region) with 2-nm band-passes. The fluorescence was observed from  $\lambda_{\text{em}} = 500\text{-}800\text{ nm}$ , depending on the excitation wavelength, at 2-nm intervals with 0.5 s integration times at room temperature.

**Relative Fluorescence Quantum Yield Measurements.** The  $\Phi_{\text{em}}$  measurements were performed using degassed toluene solutions of **1**, **1-Al**, **1-Ga**, and tetraphenylporphyrin (as a standard). Samples were excited at  $\lambda_{\text{ex}} = 355\text{ nm}$  and the emission was observed from  $\lambda_{\text{em}} = 500\text{-}800\text{ nm}$ . The standard tetraphenylporphyrin was excited at  $\lambda_{\text{ex}} = 514\text{ nm}$  and the emission was observed from  $\lambda_{\text{em}} = 500\text{-}800\text{ nm}$ .  $\Phi_{\text{em}}$  for tetraphenylporphyrin is 0.11.<sup>3</sup> All relative fluorescence quantum yields were calculated based on the corresponding fluorescence spectra of

$$\Phi_{\text{em}}(\text{x}) = \frac{A_{\text{s}} \cdot F_{\text{x}} \cdot \eta_{\text{x}}^2 \Phi_{\text{em}}(\text{s})}{A_{\text{x}} \cdot F_{\text{s}} \cdot \eta_{\text{s}}^2}$$

the samples and the standard according to the equation<sup>4-6</sup>:

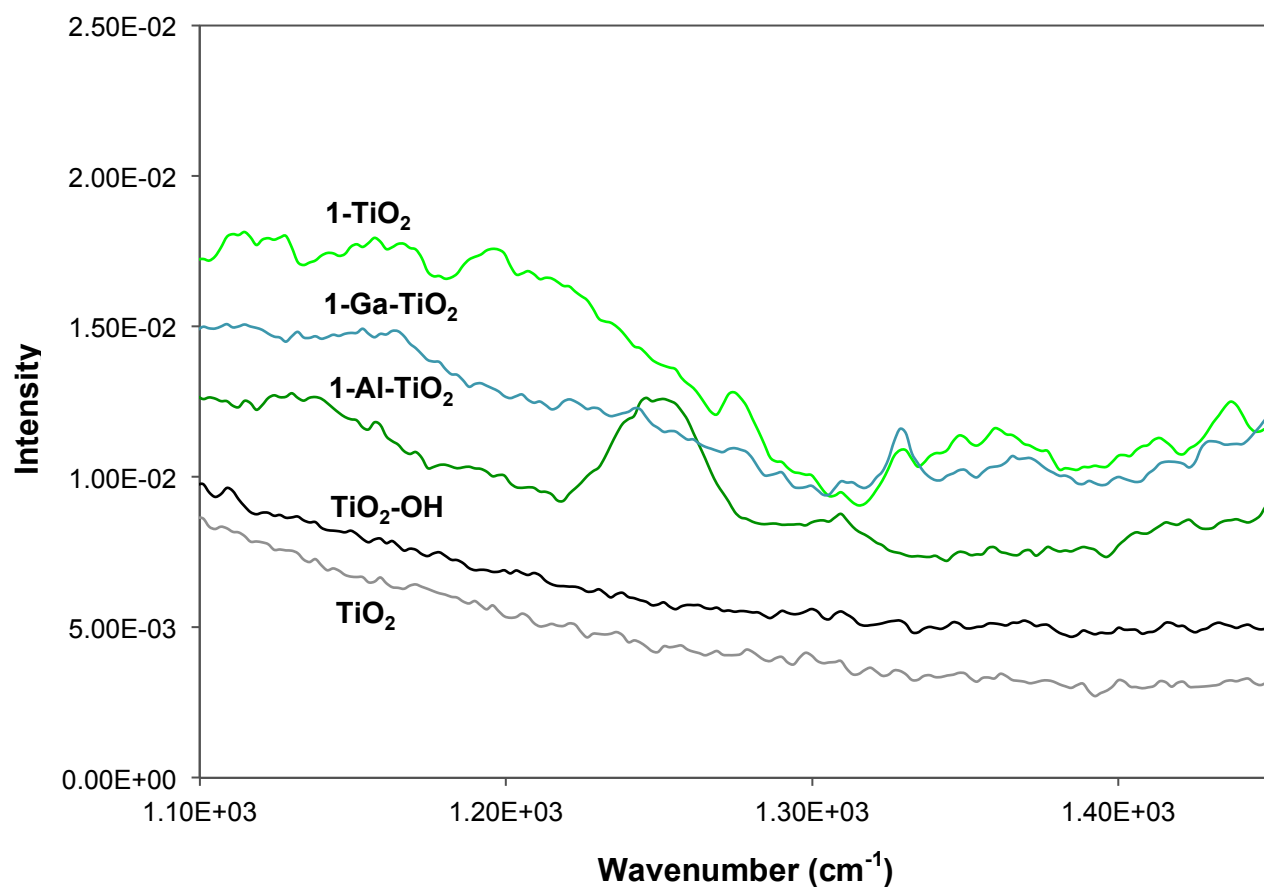
where  $\Phi_{\text{em}}(\text{s})$  and  $\Phi_{\text{em}}(\text{x})$  are the relative fluorescence quantum yield of the standard and sample, respectively;  $A_{\text{s}}$  and  $A_{\text{x}}$  are the absorbance at the excitation wavelength for the standard and sample, respectively;  $F_{\text{s}}$  and  $F_{\text{x}}$  are the area under the corrected emission curve for the standard and sample, respectively; and  $\eta_{\text{s}}$  and  $\eta_{\text{x}}$  are the refractive index of the solvent used for the standard and sample, respectively.

**Mass Spectrometry.** Samples were analyzed by direct infusion ESI in the negative ion mode using an LCT Premier XE (Waters) ESI-TOF mass spectrometer operated in the W configuration. The samples were prepared in  $\text{CH}_2\text{Cl}_2$ :isopropanol (9:1 v/v) at  $\approx 10\text{ }\mu\text{M}$  and infused with an external syringe pump at  $25\text{ }\mu\text{L}/\text{min}$ . Some samples contained  $50\text{ }\mu\text{L}$  pyridine in  $1\text{ mL}$   $\text{CH}_2\text{Cl}_2$ :isopropanol mixture.

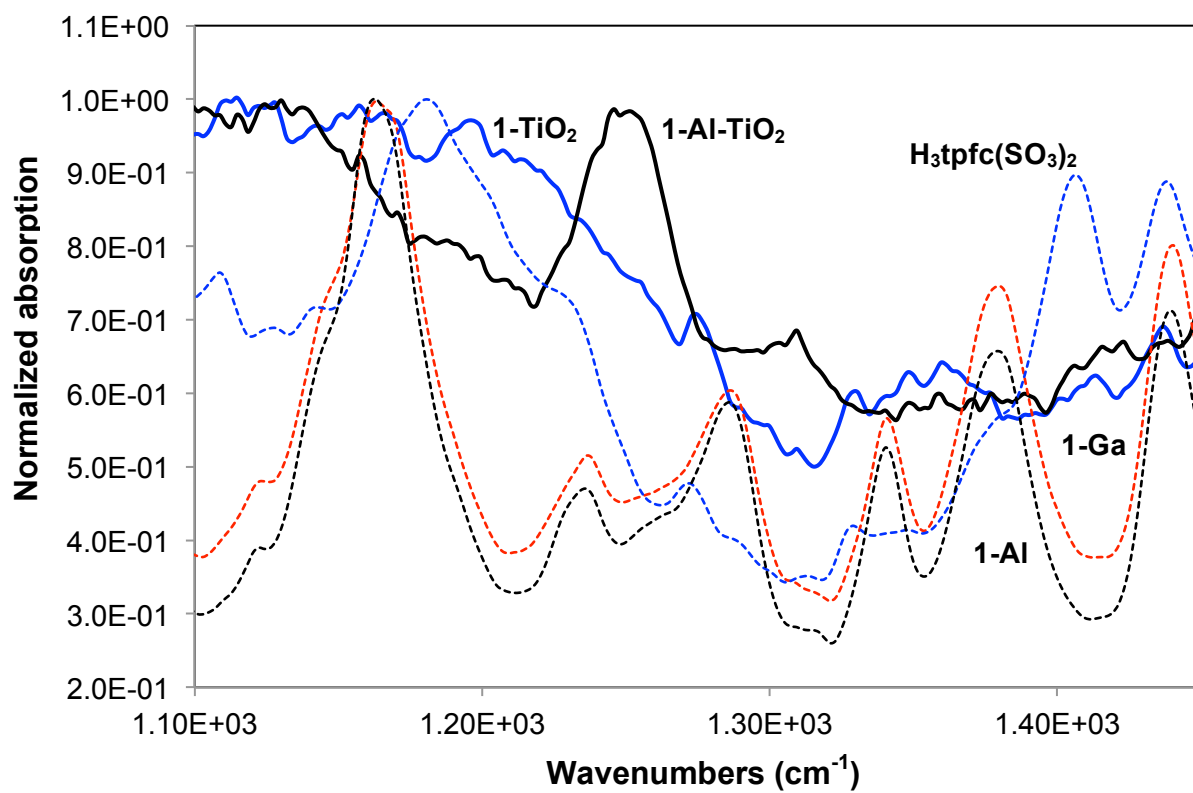
**Surface characterization.** X-ray photoelectron spectroscopy was performed on an M-Probe spectrometer that was interfaced to a computer running the ESCA2005 (Service Physics) software. The monochromatic X-ray source was the  $1486.6\text{ eV}$  Al K $\alpha$  line, directed at  $35^\circ$  to the sample surface. Emitted photoelectrons were collected by a hemispherical analyzer that was mounted at an angle of  $35^\circ$  with respect to the sample surface. Low-resolution survey spectra were acquired between binding energies of 1 and  $1100\text{ eV}$ . Higher-resolution detailed scans, with a resolution of  $\approx 0.8\text{ eV}$ , were collected on the F(1s) XPS line. All binding energies are reported in electronvolts.

Attenuated total reflectance (ATR) infrared spectra of powdered corrole-TiO<sub>2</sub> nanoconjugate samples were collected using a SensIR Durascope ATR accessory plate on a Nicolet Magna-IR spectrometer, an uncooled pyroelectric deuterated triglycine sulfate (DTGS) detector with a KBr window (400–4000 cm<sup>-1</sup>), and a KBr beamsplitter. The spectral resolution was 4 cm<sup>-1</sup> and 64 scans were collected per spectrum. A KBr background spectrum was subtracted from the measured spectrum of the nanoconjugates to provide the desired FTIR characterization data.

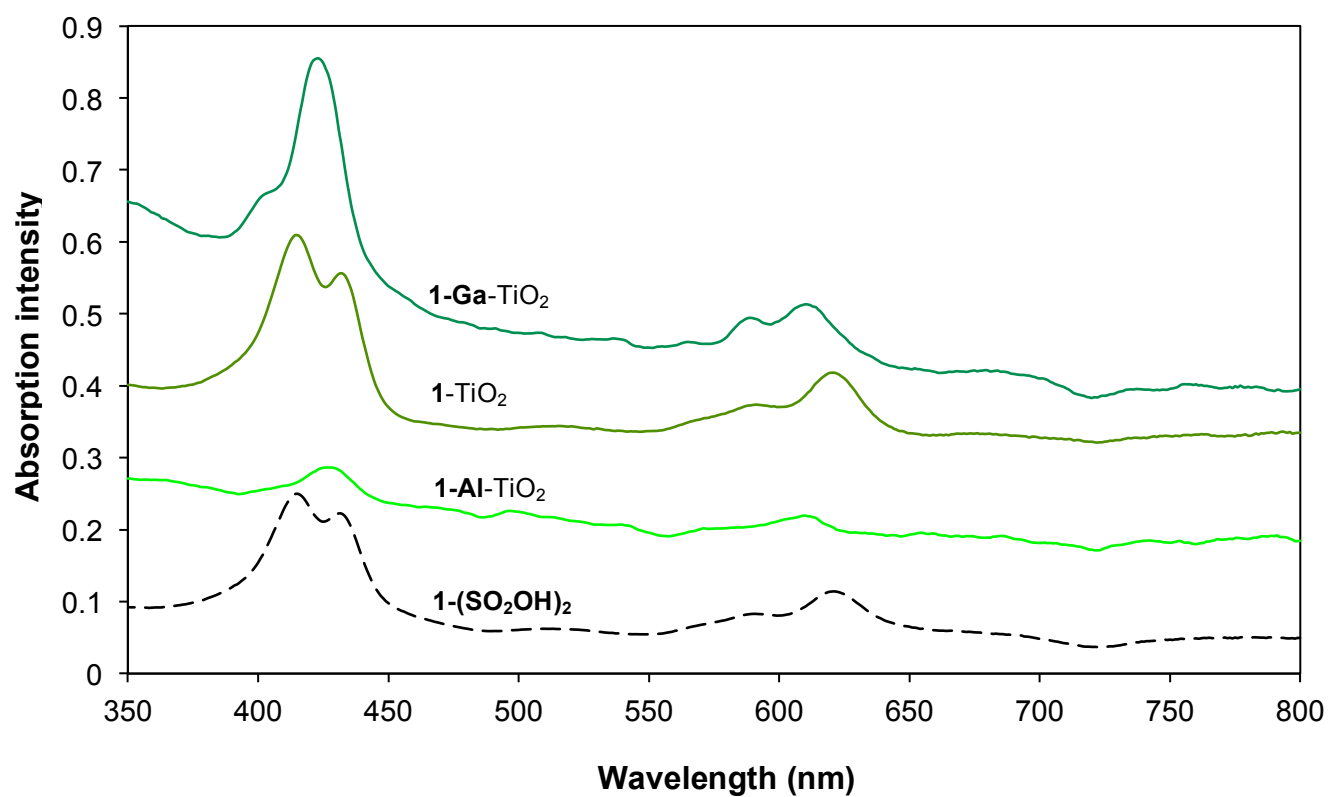
**Confocal Microscopy.** The phantom imaging experiments were performed using a Zeiss LSM 710 Confocal Microscope (Carl Zeiss, Wake Forest, NC). The microscope system consists of a Zeiss 710 confocal scanner, 63×/1.4 Plan-APOCHROMAT oil immersion lens (Zeiss), Axio Observer Z1 microscope and diode-pump solid-state lasers. Two visible excitation lines (405 and 561 nm) were used for the experiments. The microscope is equipped with a QUASAR 32 channel spectral detector (two standard PMTs and a 32 channel PMT array) with spectral resolution of 9.7 nm. The software ZEN 2009 was used for hardware control. The laser power used for the experiments is 10% of the total available power (25 mW). ImageJ software was employed to process the resulting data.



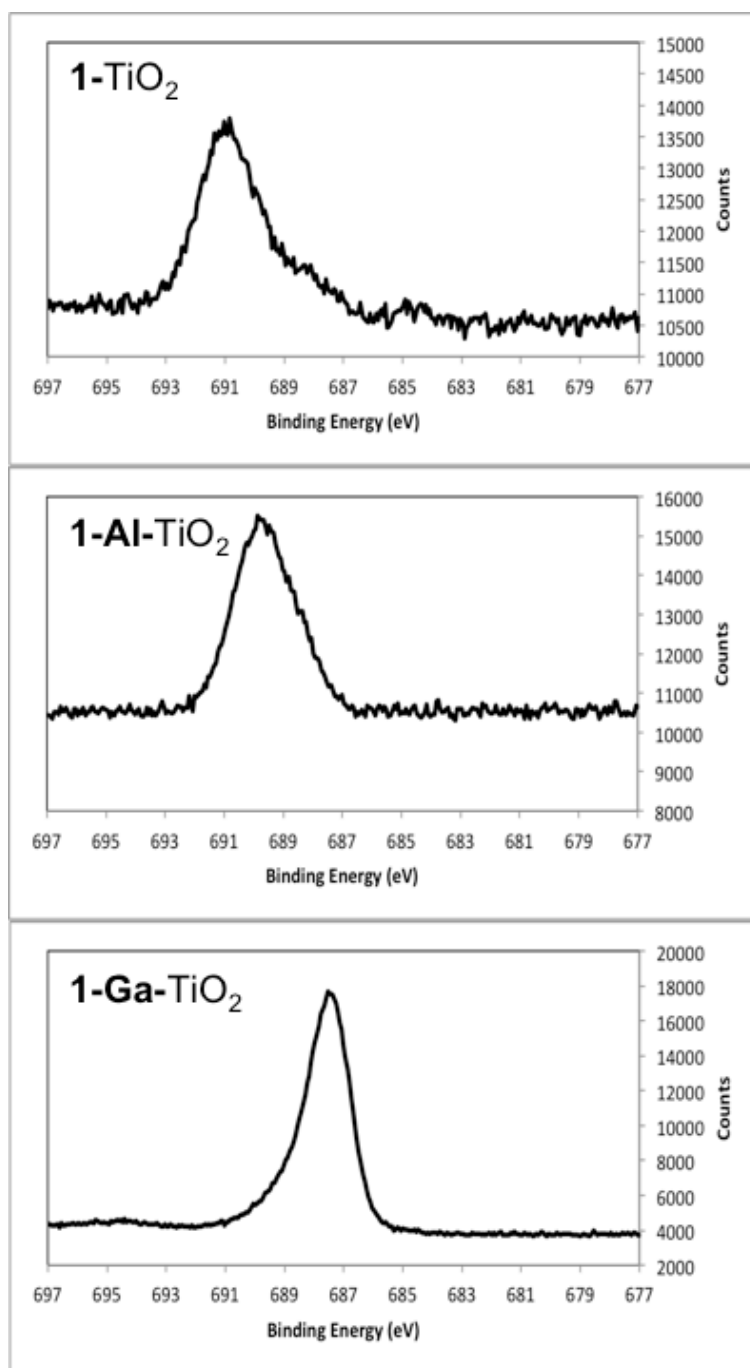
**Figure 1SI.** ATR-IR spectra for the nanoconjugates and TiO<sub>2</sub> nanoparticles.



**Figure 2SI.** Normalized ATR-IR spectra for the corrole-TiO<sub>2</sub> nanoconjugates and various corroles.



**Figure 3SI.** Electronic absorption spectra for the amphiphilic corrole ( $\text{H}_3\text{tpfc}(\text{SO}_2\text{OH})_2$ ) and the corrole-TiO<sub>2</sub> nanoconjugates in phosphate buffer saline pH 7.4.



**Figure 4SI.** X-ray photoelectron spectra for nanoconjugates **1-TiO<sub>2</sub>**, **1-Al-TiO<sub>2</sub>**, and **1-Ga-TiO<sub>2</sub>** exhibiting the F(1s) band.



Reference:

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